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INFRARED REFLECTIVITY OF IRON OXIDE MINERALS

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INTRODUCTION

From his work on the polarization of reflected light from the surface of the planet Mars Dollfus (1961) has concluded that a hydrated iron oxide known as limonite is a likely constituent of the Martian surface. Even if this material is present as only a thin surface layer the reflectivity will enter into any spectral measurements made in the region where reflected solar radiation is predominant over emitted thermal radiation. For this reason total reflection measurements have been made on a number of minerals of the iron oxide family.

Experimental Method

The total reflectivity of the minerals was measured by two separate instruments. Reflectivities from 0.5 to 2.5 microns were measured with a Beckman DK 2A double beam spectrometer equipped with a magnesium oxide coated integrating sphere. Reflectivities from 2.5 to 22.5 microns were measured with a Cary 90 double beam spectrometer equipped with the reflectance attachment described by White (1964). In all but one case, only the results from 0.5 to 6.0 microns have been reported since thermal energy would be expected to predominate beyond 5 to 6 microns from Mars.

In order to determine the influence of particle size on reflectivity all samples were crushed and then sized by a set of U.S., Standard Sieves. The sieves used had openings of 4.0, 2.0, 1.0, 0.500, 0.250, and 0.105 mm.

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All of the samples used are in the mineral collection of the U. S. National Museum in Washington, D. C., and their museum specimen number is included in the description of the samples.

RESULTS

The first group of specimens examined were of the mineral commonly known as limonite. It should be noted that the term limonite is not sufficiently specific to allow comparison of results of different investigators using different specimens. The major constituent of limonite is the mineral goethite ($HFeO_2$) with varying impurities. All specimens used have been analysed to determine their constituents and the results shown in Table 1.

Figure 1 shows the reflectivity of various size particles of Specimen No. 109590. This is a soft, yellow ocher mineral with no particles larger than 1 mm in size. The reflectivity of this sample exhibits a strong dependence on particle size in the vicinity of 2 microns and a relatively high reflectivity in this region, especially in the smaller size particles. The smaller size particles are seen to have a higher reflectivity throughout most of the spectral region shown except for some departure from this behavior between 5 and 6 microns.

The effect of water of hydration of the mineral is clearly seen with the most prominent feature in the 2.7 to 3 micron region corresponding to the ν_1 and ν_3 fundamentals of H_2O.

The weaker but still persistent feature at approximately 0.9 microns is apparently also due to water of hydration as it is greatly reduced when the mineral is dehydrated.

Figure 2 shows the reflectivity of Specimen No. 109592 described as brown, massive. It occurs as hard masses and considerable effort is necessary to reduce it to the smaller sizes. The reflectivity has many of the characteristics of the previous specimen including the minima at 0.9 and 3 microns. In addition, the features at 2.0 and 2.4 microns are of special interest in that they correspond closely to the features described by Bottema, et al (1964) seen in reflection from an ice crystal cloud.

Figure 3 shows the reflectivity of Specimen No. 18274. This specimen is similar to Specimen No. 109590 in that it is soft and yellow in color. Again the effects of water of hydration and particle size are seen very similar to the previous two specimens.

All three of the specimens described above could properly be as limonite but they are different in appearance and reflectivity illustrating the problems that can result from the use of too general a term.

Figure 4 shows the reflectivity of Specimen #4608. The specimen is a hydrated manganese oxide included to illustrate that the water of hydration feature cannot be detected when the overall reflectivity of the specimen is low.

Figure 5 shows the reflectivity of Specimen No. 109591, a mixture of magnetite (Fe_3O_4) and hematite (Fe_2O_3) with a considerable quartz impurity. The features due to water of hydration are weak since this mineral is not highly hydrated. The dependence of reflectivity on particle size is not as clearly defined as in the hydrated iron oxides. The reflectivity curves of the various size particles are seen to cross several times though in general the reflectivity is still reduced as particle size is increased.

This particular specimen shows a marked residual ray effect due to the quartz impurity but as seen in Figure 6 the strength of the feature is not clearly related to the size of the particles. It is probable that the quartz is selectively filtered so that it is not in the same proportion in each sized specimen but it should be noted that the dependence on particle size is not the same for the several features.

Figure 7 shows the reflectivity of Specimen No. 65102, a relatively pure magnetite. The overall reflectivity is low but the feature due to water of hydration can still be seen though weakly since this specimen is not highly hydrated. Virtually no change occurs in reflectivity once the particles exceed 0.5 mm in size so these curves have been omitted.

Figure 8 shows the reflectivity of Specimen No. 43621, a specimen of hematite of great purity for a naturally occurring mineral. Some water of hydration is present as evidenced by the feature at 3 microns and the dependence on particle size is seen to be fairly good in the 2 micron region.

CONCLUSIONS

The reflectivities of the various iron oxides show a dependence on particle size in the 2 micron region that is more highly pronounced in the highly reflecting hydrated specimens. If the upper layer of the Martian surface is composed of hydrated iron oxides, this dependence could allow a determination of the particle size in this layer. Though the layer accessible to infrared examination is thin, it is this layer that most seriously influences the spectral measurements of the atmosphere. Any attempt to assess atmospheric constituents by low resolution spectroscopy in the infrared must include a correction for surface reflectivity. The individual lines of the molecular vibration-rotation spectrum do not appear in solid specimens in reflectivity at temperatures reasonable for the surface of Mars so high resolution spectra will not be so restricted.

The identification of water of hydration in the upper layer of the Martian surface should be possible with an experiment such as that performed by Bottema et al (1964) on Venus. Since the atmospheric water vapor concentration is reasonably well known, its effect could be subtracted from even a low resolution spectrum and an estimate made of degree of surface hydration. All hydrated minerals examined have shown the feature at 3 microns when their overall reflectivity was reasonably high so this technique is not limited to the hydrated iron oxides.

In order to accurately assess particle size and water of hydration from reflection spectra, a careful calibration must be done to insure accurate quantitative measurements. A non-quantative

spectrum would clearly be of little use in determining particle size. The reflectivity of Specimen No. 4608 illustrates that a heavily hydrated mineral could easily be mistaken for anhydrous material from a purely relative spectrum. This work, as have many others, clearly illustrates the urgent need for further spectral data taken from outside the obscuring effect of the atmosphere of Earth.

CAPTIONS OF FIGURES

Figure 1 Reflectivity of Specimen No. 109590

Figure 2 Reflectivity of Specimen No. 109592

Figure 3 Reflectivity of Specimen No. 18274

Figure 4 Reflectivity of Specimen No. 4608

Figure 5 Reflectivity of Specimen No. 109591

Figure 6 Residual Rays of Specimen No. 109591

Figure 7 Reflectivity of Specimen No. 65102

Figure 8 Reflectivity of Specimen No. 43621

REFERENCES

Dollfus, A. (1961) Polarization Studies of Planets in "The Solar System" (G. P. Kuiper and B. M. Middlehurst, eds.) Volume 3, Chapter 9, pp 343-399, University of Chicago Press, Chicago, Illinois.

Bottema, Murk; Plummer, William; Strong, John; and Zander, Rodolphe (1964) "Composition of the Clouds of Venus," Astrophysical Journal Volume 140, No. 4, 1640-1641.

White, John U. (1964) "New Method for Measuring Diffuse Reflectance in the Infrared" J.O.S.A., Volume 54, 1332-1337.

TABLE 1

U.S.N.M. Specimen No.	Locality of Origin	Iron Oxide Minerals	Percent other Minerals	Other Minerals
109590	Cartersville, Georgia	Goethite	27	More than 90% quartz, minor mica group minerals
109592	Alabama	Goethite	5.3	Quartz
18274	Caracas, Venezuela	Goethite	47	More than 90% quartz
4608	S. Wallingsford, Vermont	Hydrous Manganese Oxides	Less than 1%	
109591	Iron Mtn., Michigan	Hematite Magnetite	44	Quartz
65102	Ontario, Canada	Magnetite	Approx. 10%	Calcite/Quartz 2:1
43621	Vermillion Lake Minnesota	Hematite	Less than 1%	

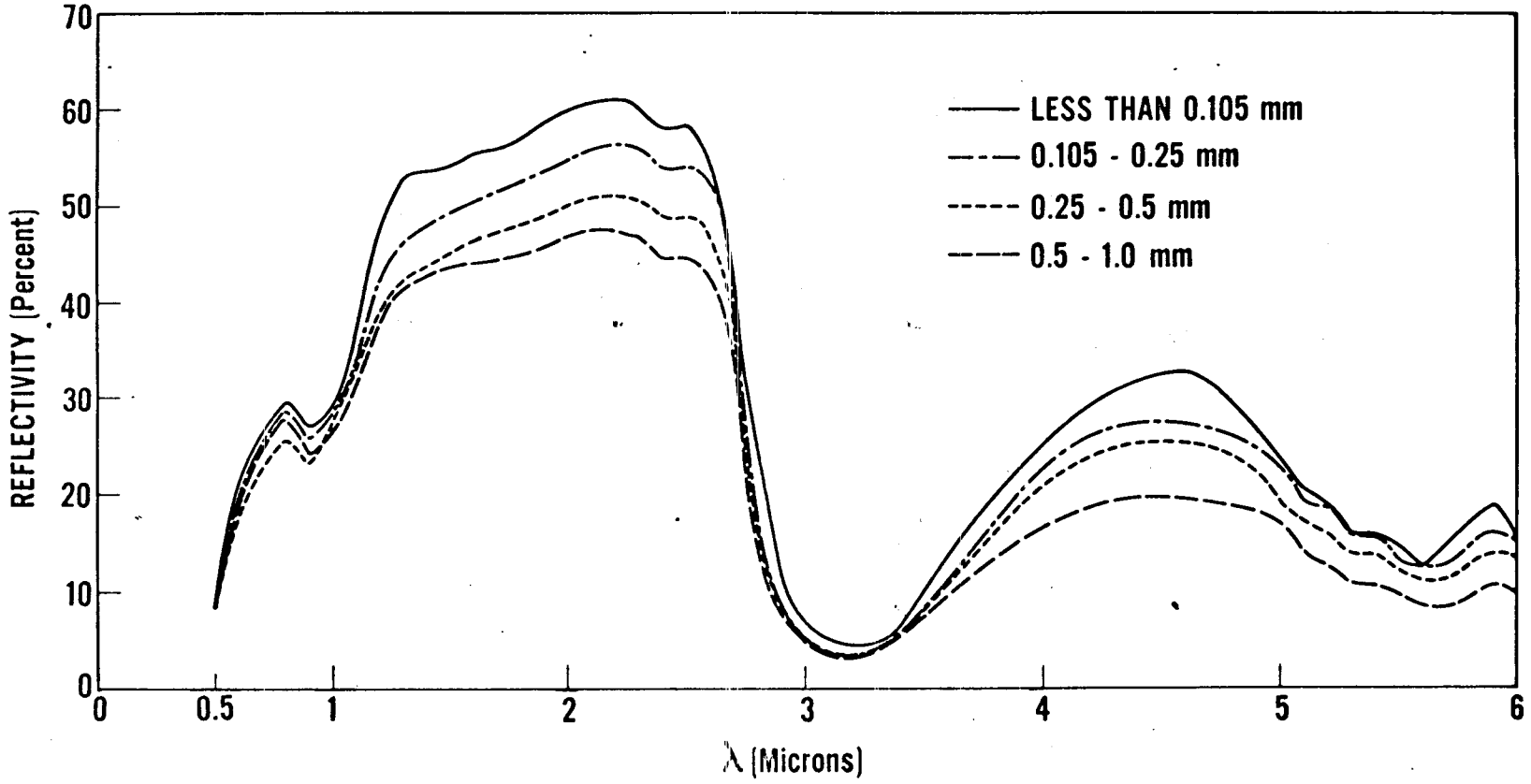
70
60
50
40
30
20
10
0
REFLECTIVITY (Percent)
0
0.5
1
2
3
4
5
6
λ (Microns)
LESS THAN 0.105 mm
0.105 - 0.25 mm
0.25 - 0.5 mm
0.5 - 1.0 mm

FIG. 1

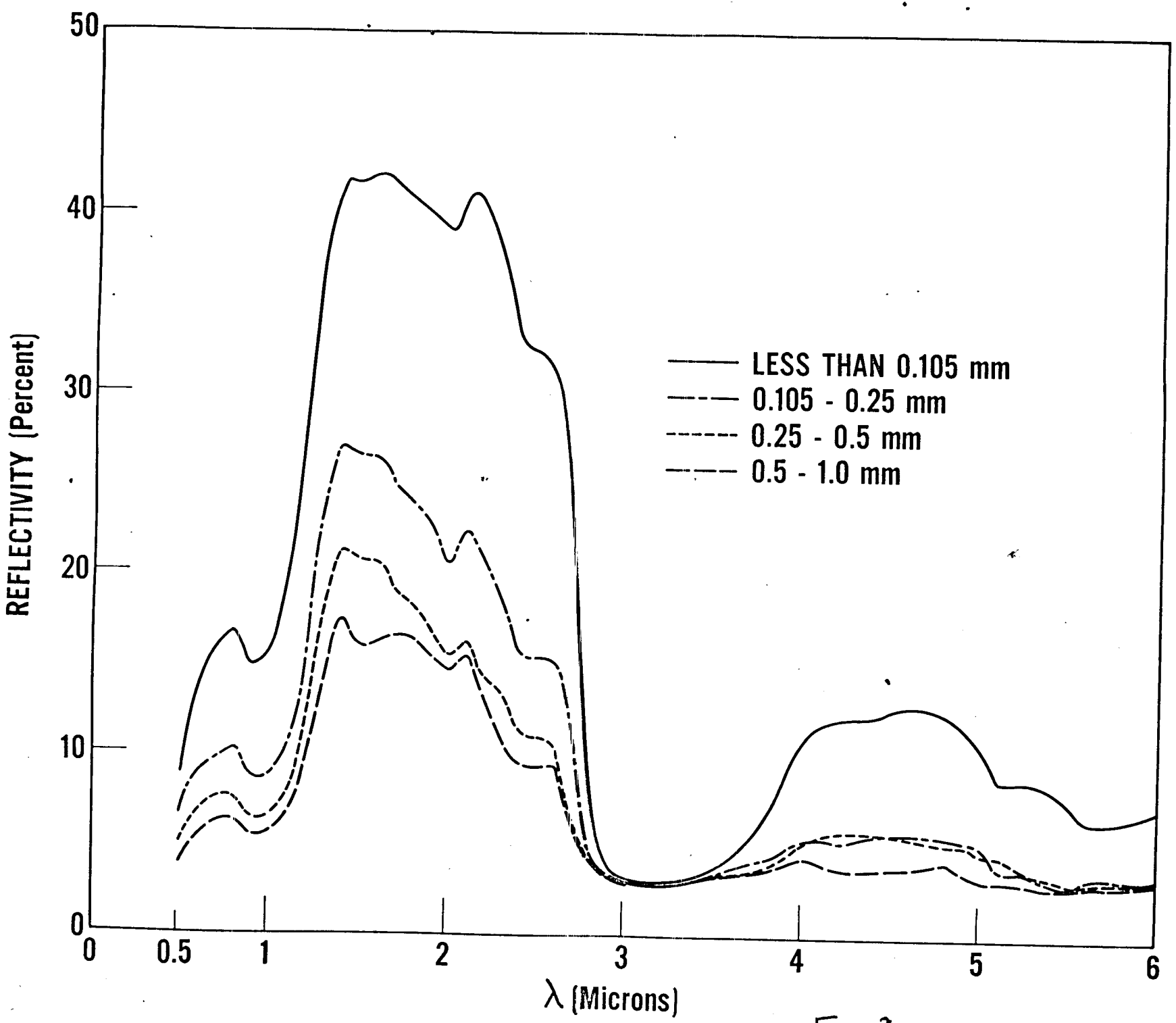
50
40
30
20
10
0
REFLECTIVITY (Percent)
0
0.5
1
2
3
4
5
6
λ (Microns)
LESS THAN 0.105 mm
0.105 - 0.25 mm
0.25 - 0.5 mm
0.5 - 1.0 mm

Fig 2

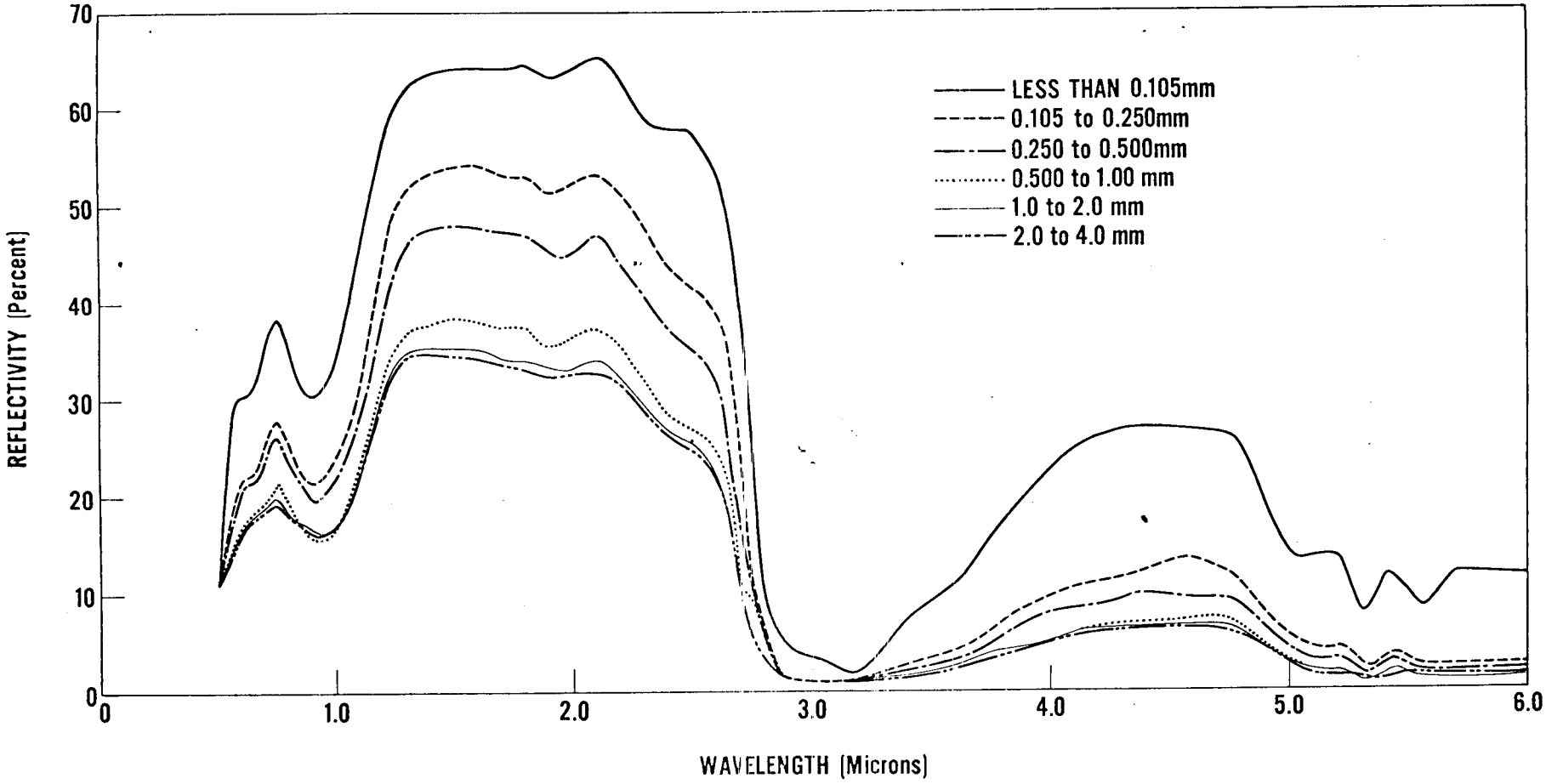
70
60
50
40
30
20
10
0
REFLECTIVITY (Percent)
0
1.0
2.0
3.0
4.0
5.0
6.0
WAVELENGTH (Microns)
LESS THAN 0.105mm
0.105 to 0.250mm
0.250 to 0.500mm
0.500 to 1.00 mm
1.0 to 2.0 mm
2.0 to 4.0 mm

Fig 3

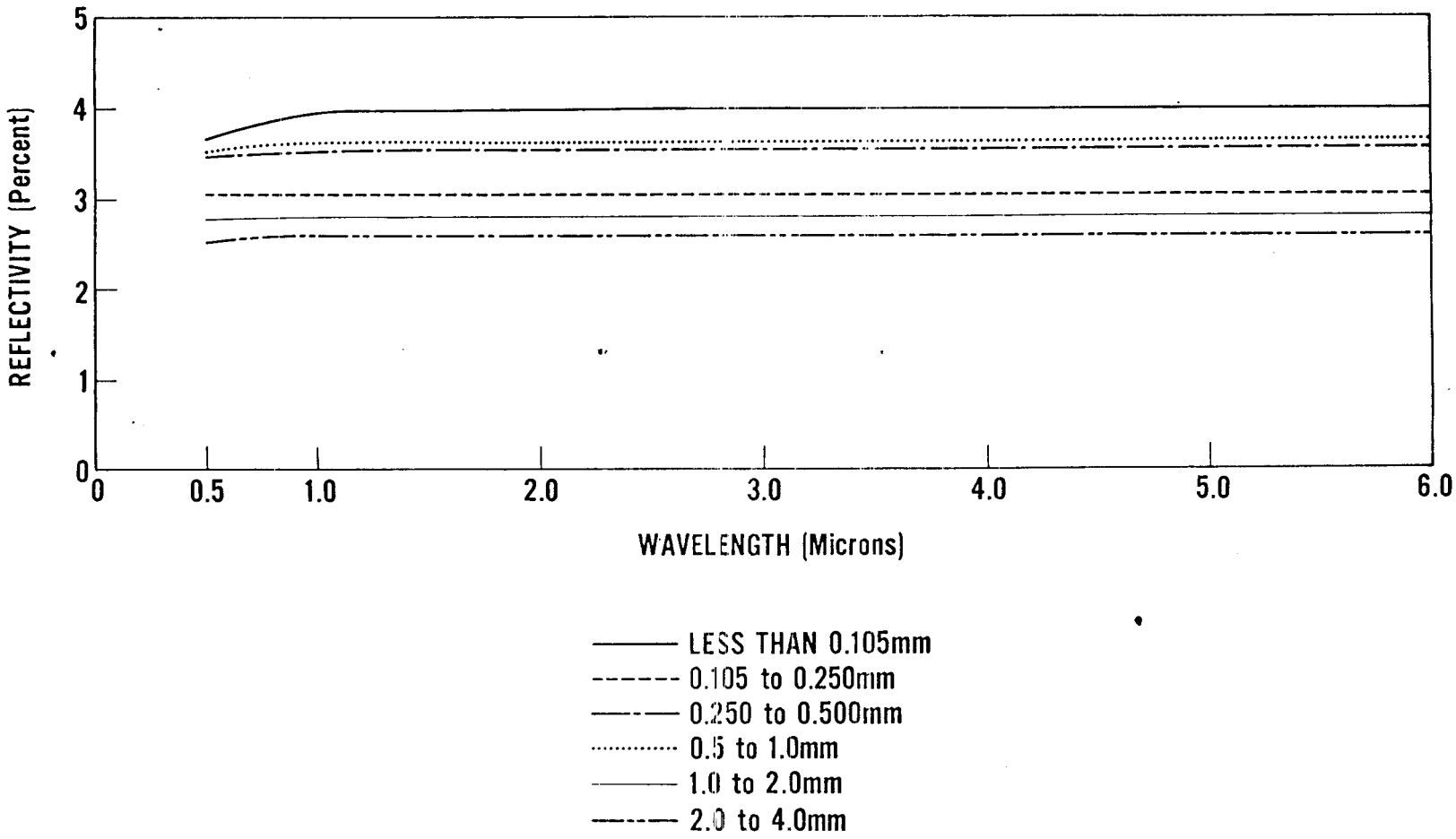
REFLECTIVITY (Percent)
5
4
3
2
1
0
0
0.5
1.0
2.0
3.0
4.0
5.0
6.0
WAVELENGTH (Microns)
LESS THAN 0.105mm
0.105 to 0.250mm
0.250 to 0.500mm
0.5 to 1.0mm
1.0 to 2.0mm
2.0 to 4.0mm

Fig 4

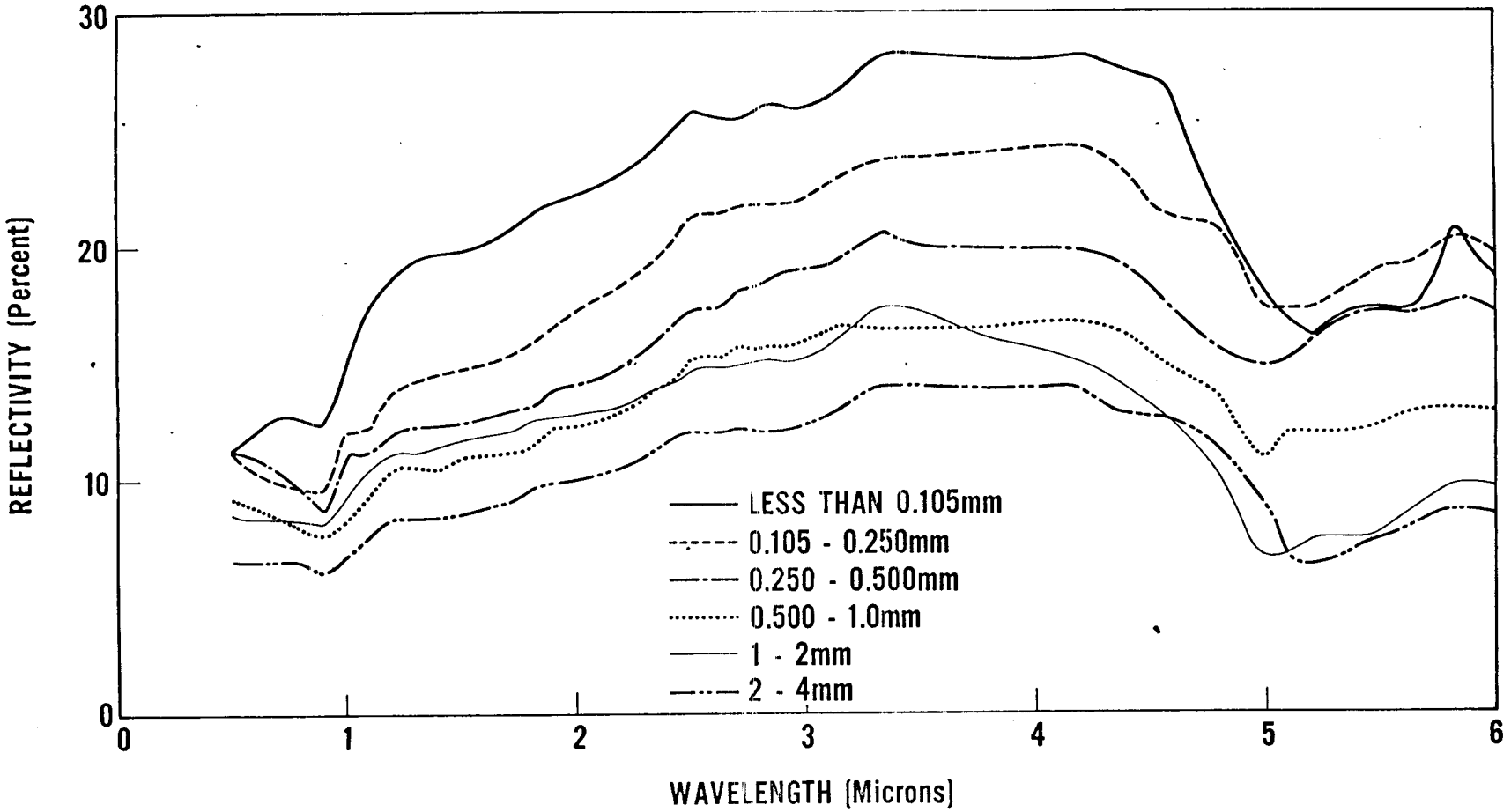
30
20
10
0
REFLECTIVITY (Percent)
0
1
2
3
4
5
6
WAVELENGTH (Microns)
LESS THAN 0.105mm
0.105 - 0.250mm
0.250 - 0.500mm
0.500 - 1.0mm
1 - 2mm
2 - 4mm

Fig 5

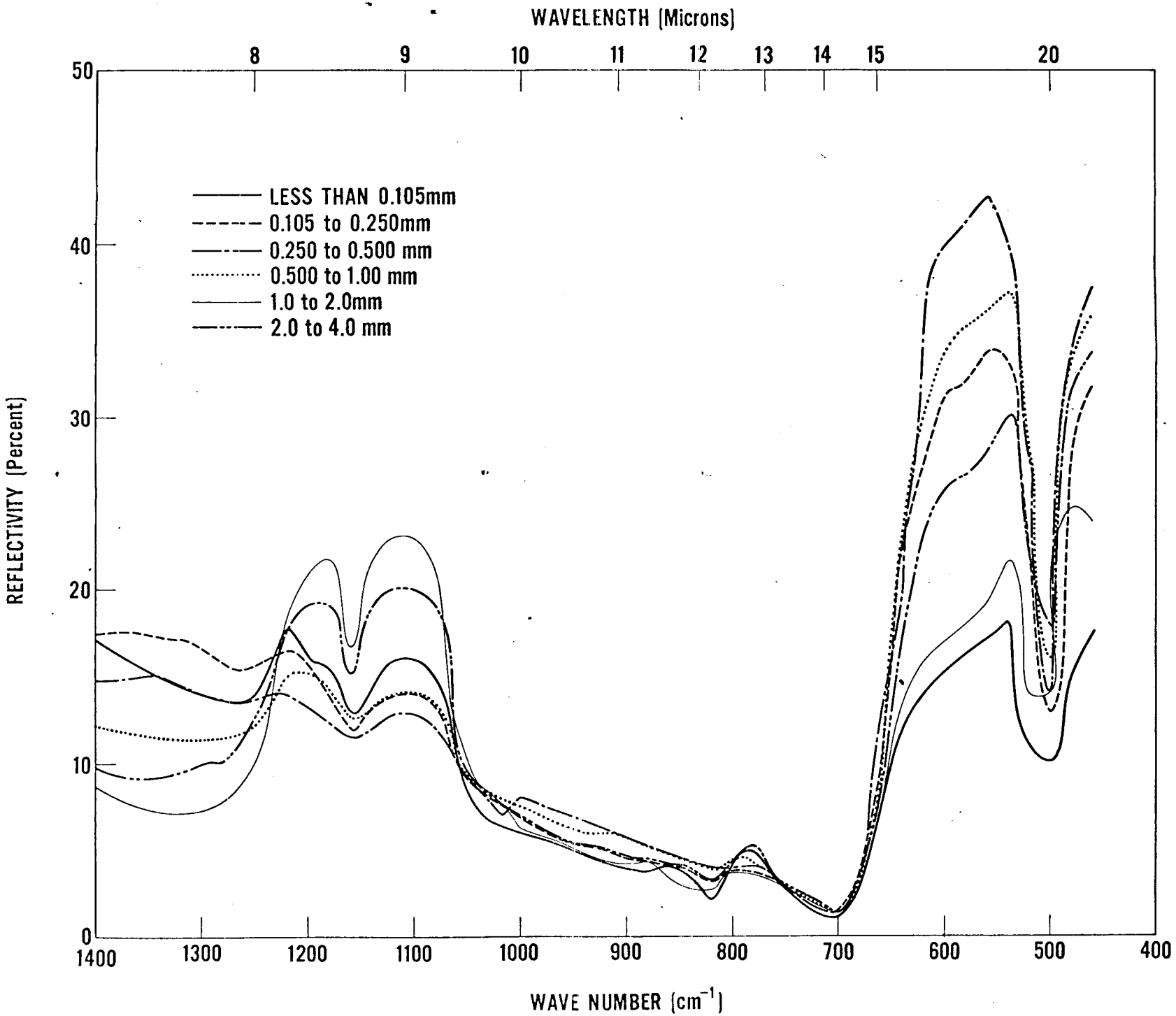
WAVELENGTH (Microns)
8
9
10
11
12
13
14
15
20
50
40
30
20
10
0
REFLECTIVITY (Percent)
LESS THAN 0.105mm
0.105 to 0.250mm
0.250 to 0.500 mm
0.500 to 1.00 mm
1.0 to 2.0mm
2.0 to 4.0 mm
1400
1300
1200
1100
1000
900
800
700
600
500
400
WAVE NUMBER (cm^{-1})

FIG 6

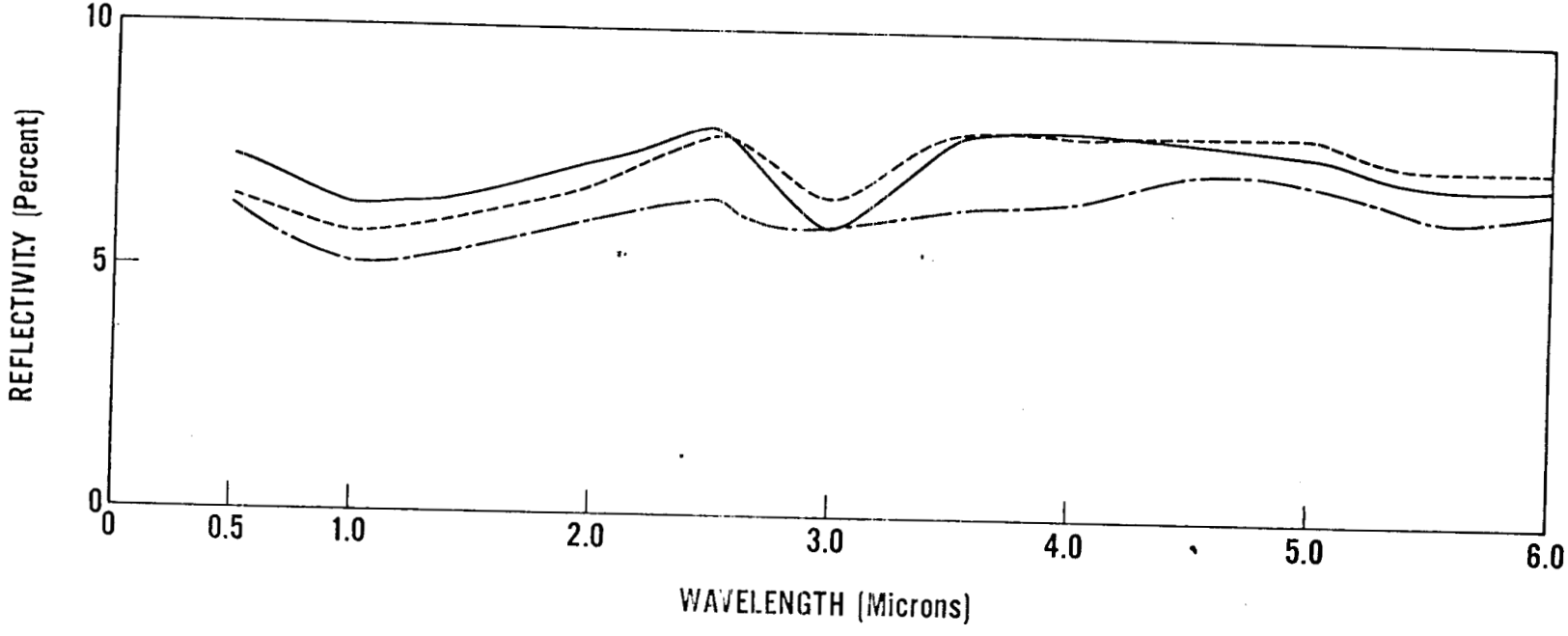
10
5
0
REFLECTIVITY (Percent)
0
0.5
1.0
2.0
3.0
4.0
5.0
6.0
WAVELENGTH (Microns)
LESS THAN 0.105mm
0.105 to 0.250mm
0.250 to 0.500mm

Fig. 7

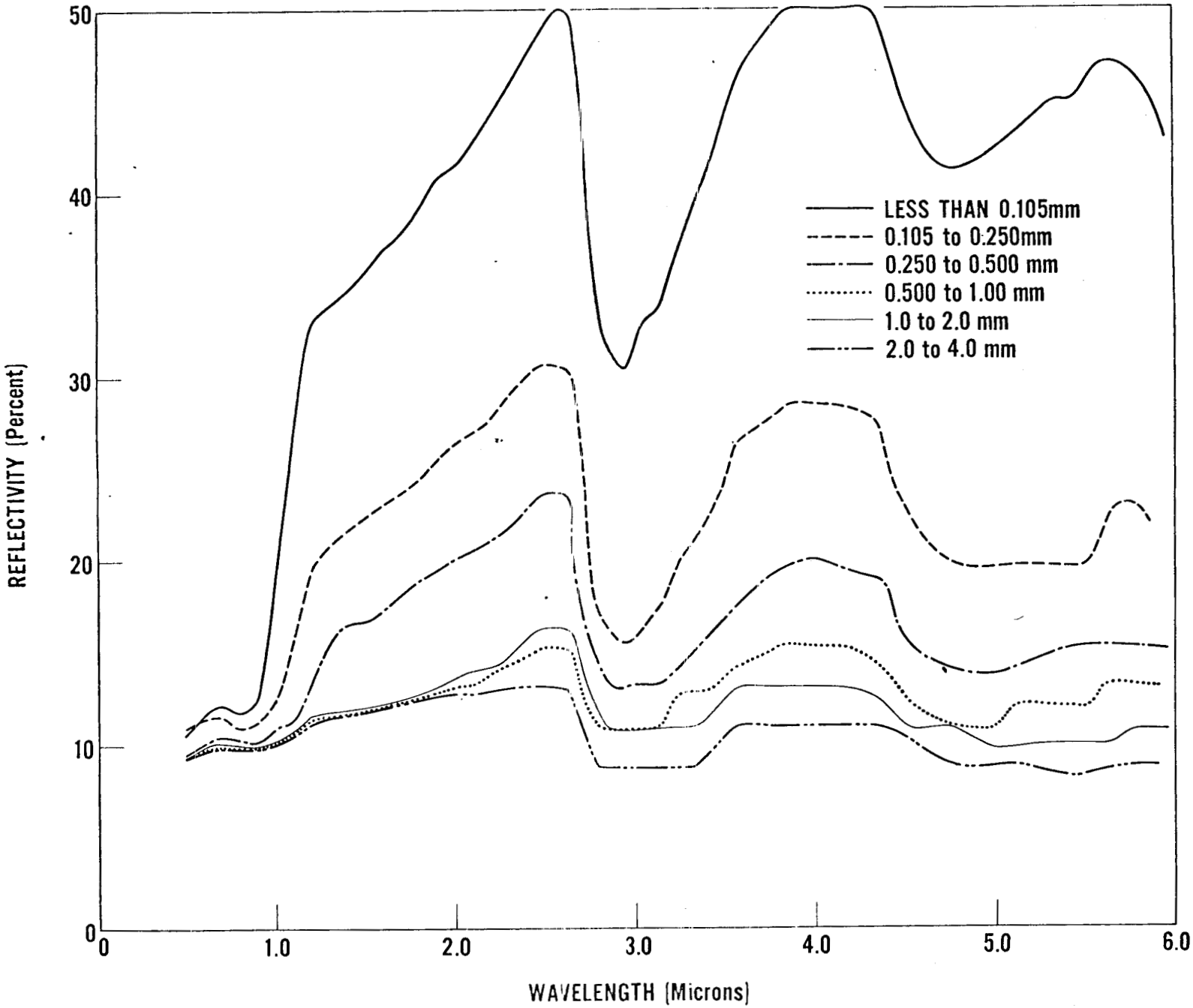
LESS THAN 0.105mm
0.105 to 0.250mm
0.250 to 0.500 mm
0.500 to 1.00 mm
1.0 to 2.0 mm
2.0 to 4.0 mm
REFLECTIVITY (Percent)
WAVELENGTH (Microns)
0
10
20
30
40
50
0
1.0
2.0
3.0
4.0
5.0
6.0

Fig 8